

5-12-2009


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Cynthia Chen
Dartmouth College

Peter N. Sedwick
Old Dominion University

Mukul Sharma
Dartmouth College

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Anthropogenic osmium in rain and snow reveals global-scale atmospheric contamination

Cynthia Chen^a, Peter N. Sedwick^b, and Mukul Sharma^{a,1}

^aRadiogenic Isotope Geochemistry Laboratory, Department of Earth Sciences, Dartmouth College, 6105 Sherman Fairchild Hall, Hanover, NH 03755; and ^bDepartment of Ocean, Earth and Atmospheric Sciences, Old Dominion University, 4600 Elkhorn Avenue, Norfolk, VA 23529

Edited by Karl K. Turekian, Yale University, New Haven, CT, and approved March 27, 2009 (received for review November 19, 2008)

Osmium is one of the rarer elements in seawater, with typical concentration of $\approx 10 \times 10^{-15} \text{ g g}^{-1}$ ($5.3 \times 10^{-14} \text{ mol kg}^{-1}$). The osmium isotope composition ($^{187}\text{Os}/^{188}\text{Os}$ ratio) of deep oceans is 1.05, reflecting a balance between inputs from continental crust (≈ 1.3) and mantle/cosmic dust (≈ 0.13). Here, we show that the $^{187}\text{Os}/^{188}\text{Os}$ ratios measured in rain and snow collected around the world range from 0.16 to 0.48, much lower than expected (> 1), but similar to the isotope composition of ores (≈ 0.2) that are processed to extract platinum and other metals to be used primarily in automobile catalytic converters. Present-day surface seawater has a lower $^{187}\text{Os}/^{188}\text{Os}$ ratio (≈ 0.95) than deep waters, suggesting that human activities have altered the isotope composition of the world's oceans and impacted the global geochemical cycle of osmium. The contamination of the surface ocean is particularly remarkable given that osmium has few industrial uses. The pollution may increase with growing demand for platinum-based catalysts.

pollution | seawater | isotopes | platinum group metals | precipitation

The introduction of automobile catalytic converters has substantially reduced emissions of NO_x , CO , and short-chained hydrocarbons over the last 30 years. However, an unintended consequence of using catalytic converters is that the platinum group elements (PGEs: Os, Ir, Pt, Pd, Ru, Rh) are now polluting the environment (1). Although most of fine particulate matter from automobile exhaust containing PGEs settles close to highways and in urban areas (e.g., refs. 2 and 3), increasing PGE concentrations have been noted in ice cores (1, 4) and snow (5–7) in remote regions. In general, all PGEs are immobile (8) except Os, which can form volatile OsO_4 during high-temperature industrial processes such as smelting of concentrated ores (9). Anthropogenic Os has been observed in estuaries (10, 11), coastal sediments (12, 13), and lakes (3). Aerially transmitted anthropogenic Os has been observed near chromium smelters (14) and in urban areas (11, 15), where likely sources are hospital incinerators (10, 16) and automobile catalytic converters (17). Smelters and incinerators represent a local contamination source, whereas automobile catalytic converters could potentially provide a much a larger source of globally dispersed Os. The key issues are the extent to which the anthropogenic Os is dispersed and whether this is impacting the natural geochemical cycle of Os. If the natural budget of Os has been disturbed by human activity, then Os isotopes could be a valuable tracer for the hydrological cycle, similar to Pb from leaded gasoline usage before 1978 or tritium from atmospheric atomic bomb testing in the early 1960s. Here, we examine these questions by measuring Os in surface waters.

Deep seawater has an Os $^{187}\text{Os}/^{188}\text{Os}$ of 1.05 ± 0.01 , reflecting a balance between riverine and cosmic and/or hydrothermal sources (18–21). Because radiogenic ^{187}Os is produced from the β -decay of ^{187}Re (half-life = 42 billion years), the $^{187}\text{Os}/^{188}\text{Os}$ of potential atmospheric sources of Os vary considerably, depending on their Re/Os and the time elapsed after their formation (Fig. 1). Os isotope compositions closer to 0.1 are considered “unradiogenic,” whereas those closer to 1 are considered “ra-

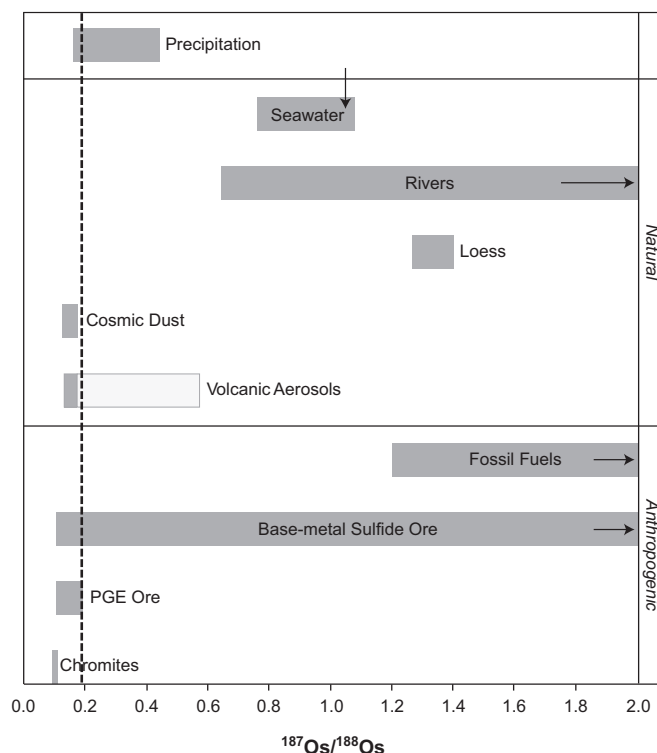


Fig. 1. Comparison of the Os isotope ratios of potential atmospheric sources with values measured in precipitation. Dashed line represents the unradiogenic endmember estimated from the y-intercept of the mixing line (Fig. 2). The arrow in seawater range marks the average $^{187}\text{Os}/^{188}\text{Os}$ ratio of deep-ocean water. The lighter box on the volcanic aerosols represents values estimated from island arc rocks. Rivers, fossil fuels, and base-metal sulfide ores have $^{187}\text{Os}/^{188}\text{Os}$ values that exceed 2. Data references are: precipitation (this study and refs. 25 and 53), seawater (this study and refs. 18–20 and 48), rivers (25, 54), loess (22, 23), cosmic dust (19, 55), volcanic aerosols (24–26), fossil fuels (27, 28), base-metal sulfide ores (30–32), PGE ores (29), and chromites (33).

diogenic.” Natural sources of Os to the atmosphere include continental mineral aerosols ($^{187}\text{Os}/^{188}\text{Os} = 1.26$) (22, 23), cosmic dust ($^{187}\text{Os}/^{188}\text{Os} = 0.13$) (19), and volcanic aerosols. There are limited data on the Os isotope composition of volcanic aerosols; direct measurements from Mauna Loa (Hawaii) give a value of 0.14 (24). However, aerosols from volumetrically dominant eruptions at the convergent margins are likely to be more radiogenic: Analyses of a large number of volcanic rocks from

Author contributions: C.C. and M.S. designed research; C.C. and P.N.S. performed research; C.C. and M.S. analyzed data; and C.C. and M.S. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹To whom correspondence should be addressed. E-mail: mukul.sharma@dartmouth.edu.

This article contains supporting information online at www.pnas.org/cgi/content/full/0811803106/DCSupplemental.

Table 1. Osmium concentrations and isotopic compositions in rain, snow, and seawater

Parameter	Coordinates	[Os], fg g ⁻¹	[Os] _c [†] , fg g ⁻¹	¹⁸⁷ Os/ ¹⁸⁸ Os [‡]	[¹⁸⁷ Os/ ¹⁸⁸ Os] _c [†]
Precipitation					
North America					
Alaska	65°9'N, 147°29'W	0.35 ± 0.01	0.28 ± 0.02	0.386 ± 0.006	0.42 ± 0.01
California (Soda Springs), snow	39°23'N, 120°27'W	2.94 ± 0.02	2.9 ± 0.1	0.204 ± 0.003	0.202 ± 0.003
Montana	45°35'N, 107°26'W	0.33 ± 0.01	0.25 ± 0.01	0.402 ± 0.006	0.441 ± 0.008
Ohio, rain	40°47'N, 80°55'W	0.600 ± 0.004	0.53 ± 0.03	0.337 ± 0.006	0.346 ± 0.005
Florida, rain	27°22'N, 82°17'W	0.931 ± 0.005	0.86 ± 0.04	0.278 ± 0.006	0.279 ± 0.006
New Hampshire (Hanover), snow	43°42'N, 72°17'W	17.0 ± 0.1	16.9 ± 0.9	0.164 ± 0.003	0.163 ± 0.002
New Hampshire (Hanover), rain	43°43'N, 72°15'W	0.993 ± 0.006	0.92 ± 0.05	0.240 ± 0.006	0.238 ± 0.004
Europe					
Almere, The Netherlands, rain	52°23'N, 5°18'E	5.31 ± 0.03	5.2 ± 0.3	0.275 ± 0.004	0.275 ± 0.004
Asia					
Mangalore, India, rain	12°54'N, 74°50'E	22.9 ± 0.3	23 ± 1	0.160 ± 0.002	0.160 ± 0.002
Antarctica					
Ross Sea (CORSACS2 IS-1), snow	67°08'S, 174°42'W	1.76 ± 0.01	1.69 ± 0.09	0.198 ± 0.003	0.195 ± 0.003
Ross Sea (CORSACS2 IS-3), snow	70°19'S, 177°07'W	0.83 ± 0.01	0.76 ± 0.04	0.46 ± 0.01	0.474 ± 0.007
Replicate		0.813 ± 0.006	0.74 ± 0.04	0.458 ± 0.007	0.477 ± 0.007
East Antarctic (SIPEX 10), brine	64°56'S, 119°09'E	11.46 ± 0.06	11.4 ± 0.6	1.02 ± 0.02	1.03 ± 0.01
East Antarctic (SIPEX 10), snow	64°56'S, 119°09'E	3.42 ± 0.02	3.4 ± 0.2	0.97 ± 0.02	0.98 ± 0.01
East Antarctic (SIPEX 11), snow	65°00'S, 117°30'E	0.81 ± 0.01	0.74 ± 0.04	0.362 ± 0.006	0.371 ± 0.005
Seawater					
Surface					
Atlantic Ocean 2007 (25 m)	31°31'N, 63°18'W	9.82 ± 0.08	9.7 ± 0.5	0.76 ± 0.01	0.76 ± 0.01
Atlantic Ocean 2008 (7 m)	31°40'N, 64°10'W	6.22 ± 0.02	6.1 ± 0.3	1.02 ± 0.01	1.03 ± 0.01
Southern Ocean 2006 (6 m)	65°13'S, 174°44'W	9.97 ± 0.08	9.9 ± 0.5	0.956 ± 0.01	0.96 ± 0.01
Indian Ocean 1997 (22 m)*	34°11'S, 55°37'E	–	11.14 ± 0.45	–	1.02 ± 0.04
Pacific Ocean 1997 (25 m)	9°46'N, 104°11'W	8.25 ± 0.10	8.2 ± 0.4	1.01 ± 0.01	1.02 ± 0.01
Deep					
Atlantic Ocean 2007 (2000 m) 20 mL	31°40'N, 64°10'W	8.98 ± 0.07	8.9 ± 0.4	1.03 ± 0.01	1.05 ± 0.01
Replicate		8.90 ± 0.07	8.8 ± 0.4	1.05 ± 0.01	1.06 ± 0.02
Atlantic Ocean 2007 (2000 m) 40 mL	31°40'N, 64°10'W	8.81 ± 0.05	8.8 ± 0.4	1.04 ± 0.01	1.05 ± 0.02
Replicate		8.96 ± 0.03	8.9 ± 0.4	1.04 ± 0.01	1.05 ± 0.02
Atlantic Ocean 2007 (2000 m) 60 mL	31°40'N, 64°10'W	8.67 ± 0.05	8.6 ± 0.4	1.04 ± 0.01	1.04 ± 0.02
Replicate		8.91 ± 0.05	8.7 ± 0.4	1.04 ± 0.01	1.05 ± 0.01
Average deep seawater		8.88 ± 0.12	8.80 ± 0.16	1.041 ± 0.006	1.051 ± 0.006

*Data from ref. 18.

†Corrected for a 3.6 ± 0.08 fg blank with $^{187}\text{Os}/^{188}\text{Os} = 0.27 \pm 0.032$. The given uncertainty reflects uncertainty in the blank determination and counting statistics (Fig. S2).

[†]Reported uncertainties are the higher of either the external reproducibility of 1.38% or 2 times the standard error from counting statistics.

island arcs suggest that the average $^{187}\text{Os}/^{188}\text{Os}$ ratio of the aerosols could be ≈ 0.53 (25), although measurements of Kudryavy volcano show gas condensates to be less radiogenic (0.122–0.152) than the volcanic rocks (0.205–0.588) (26).

Potential anthropogenic sources of Os to the atmosphere include: (i) combustion of fossil fuels, (ii) smelting of PGE sulfide ores, (iii) smelting of base-metal (Cu, Ni, Zn, and Pb) sulfide ores, (iv) smelting of chromium ore, and (v) exhaust from automobile catalytic converters (17). Published $^{187}\text{Os}/^{188}\text{Os}$ ratios for fossil fuels are highly radiogenic, ranging from 1.2 to 13.7 (27, 28). In contrast, the $^{187}\text{Os}/^{188}\text{Os}$ of the PGE sulfide ores from the Bushveld Complex, South Africa, are between 0.15 and 0.20 (29). The $^{187}\text{Os}/^{188}\text{Os}$ of base-metal sulfide deposits are variable: in some cases they are similar to the PGE ores [e.g., Noril'sk, Russia (30), and Yilgarn craton, Australia (31)], and in other cases they are highly radiogenic because of involvement of continental crust in their formation [e.g., Sudbury, Canada (32)]. Chromites of all ages have uniformly low $^{187}\text{Os}/^{188}\text{Os}$ values, ranging from 0.12 to 0.14 (33). The majority of PGEs are produced in South Africa (Bushveld Complex; $\approx 70\%$) and Russia (Noril'sk; $\approx 25\%$) (34), therefore the $^{187}\text{Os}/^{188}\text{Os}$ of automobile exhaust is expected to be 0.15–0.20; direct measurements from catalytic converters give 0.1–0.2 (17).

Results

We measured Os in precipitation samples from North America, Europe, Asia, and Antarctica, and in surface and deep seawater from the North Atlantic, Pacific, and Southern Oceans (Table 1). Os concentrations in precipitation range from 0.25 to 23 fg g⁻¹, averaging 5.7 fg g⁻¹ (1 fg = 10⁻¹⁵ g). The ¹⁸⁷Os/¹⁸⁸Os ratios of these samples are relatively low (0.16–0.48), and fall along a 2-component mixing line (Fig. 2). Several Antarctic snow samples deviate from the mixing line, but this shift to more radiogenic values is likely because of contamination of the snow by brine within the sea ice, because samples with higher salinities have Os concentrations and ¹⁸⁷Os/¹⁸⁸Os ratios closer to those of brine samples. The mixing line in Fig. 2 requires that one source of Os in precipitation to be relatively concentrated with an isotope composition of ¹⁸⁷Os/¹⁸⁸Os ≈ 0.19, whereas the other Os source would be relatively dilute with ¹⁸⁷Os/¹⁸⁸Os ≥ 0.48. If the radiogenic endmember were continental mineral dust [¹⁸⁷Os/¹⁸⁸Os = 1.26; (22, 23)], the isotope mass balance indicates that >95% of Os in rain is derived from the unradiogenic source. The ¹⁸⁷Os/¹⁸⁸Os ratios of the surface seawater samples range from 0.76 to 1.03, lower than those measured in deep (≥2,000 m) ocean water, 1.05 ± 0.01 (Table 1 and refs. 18–20). The estimated average ¹⁸⁷Os/¹⁸⁸Os of surface seawater is 0.95. If the

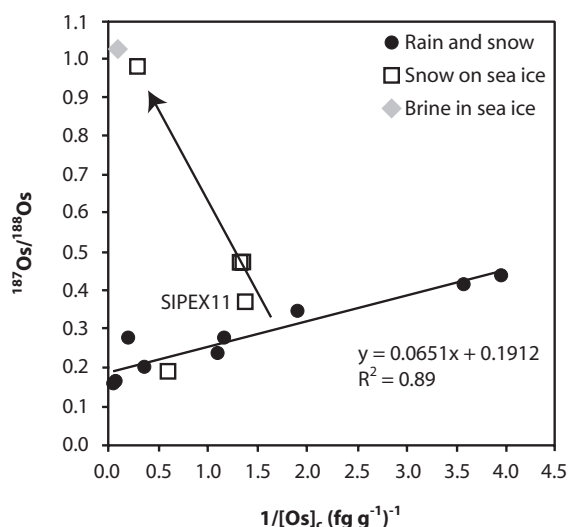


Fig. 2. Plot of $^{187}\text{Os}/^{188}\text{Os}$ versus reciprocal of $[\text{Os}]$ defines a 2-component mixing line for the precipitation data. The unradiogenic endmember has an isotope composition of ≈ 0.19 . Snow collected from sea ice falls on another mixing line between brine and the precipitation mixing line, suggesting that the snow samples are contaminated with brine.

radiogenic endmember in Fig. 2 were surface seawater, the isotope mass balance indicates that $>90\%$ of Os in rain is derived from the unradiogenic source.

Discussion

The low $^{187}\text{Os}/^{188}\text{Os}$ of precipitation implies that sources of highly radiogenic Os cannot contribute the bulk of the Os in precipitation (Fig. 1). Natural sources of unradiogenic Os include meteorites/cosmic dust and volcanism, whereas anthropogenic sources involve processing of sulfide, chromium, and PGE ores and exhaust from automobiles. In the following sections, we examine each of these sources and infer that Os produced during refining of PGE ores likely dominate the isotope signal in precipitation. We then discuss the impact of anthropogenic Os on surface waters.

Natural Sources of Osmium to Precipitation. Cosmic dust and meteorites are unradiogenic (Fig. 1). By using an estimated accretion rate of $0.2\text{--}1.7\text{ g y}^{-1}$ (21), an annual precipitation rate of $5 \times 10^{20}\text{ g y}^{-1}$ (35), and assuming complete dissolution of the cosmic dust, the expected Os concentration of precipitation is $4\text{--}34 \times 10^{-7}\text{ fg g}^{-1}$. The maximum concentration ($34 \times 10^{-7}\text{ fg g}^{-1}$), is much lower than our lowest measured concentration (0.25 fg g^{-1}) for Montana rain. The impact of extraterrestrial Os on the composition of Antarctic snow could be greater if extraterrestrial particles are focused to polar regions (36). The estimated flux of Ir to Antarctica is $4\text{ fg cm}^{-2}\text{ y}^{-1}$ (36). Assuming the Os/Ir ratio of cosmic dust is ≈ 1 and using a net snow accumulation rate of $\approx 30\text{ cm y}^{-1}$ for snow on sea ice, the Os concentration in snow should be $\approx 0.13\text{ fg cm}^{-3}$ ($=\text{ fg g}^{-1}$). However, 0.13 fg g^{-1} is only 18% of the total Os found in our least-concentrated Antarctic snow, SIPEX11 (0.74 fg g^{-1} ; Fig. 2). If Os in SIPEX11 were only a mixture of extraterrestrial dust and seawater, the isotopic mass balance suggests that its $^{187}\text{Os}/^{188}\text{Os}$ would be 0.88. This is much higher than the ratio of 0.37 measured in the SIPEX11 snow. It follows that there must be an additional source of unradiogenic Os to Antarctic snow besides extraterrestrial dust.

That subaerial volcanic activity may provide aerosols with unradiogenic Os is supported by direct measurements of Os isotopes in volcanic emissions from Mauna Loa, Hawaii (24).

The Os isotope composition from Mauna Loa may not be globally representative as the volcanism is associated with hot-spot activity, which contributes only $\approx 5\%$ of total volcanic SO_2 (37). Subduction-zone volcanoes are responsible for $\approx 80\%$ of volcanic SO_2 . Measurements of gas condensate from Kudryavy found them to have lower $^{187}\text{Os}/^{188}\text{Os}$ than the unaltered volcanic rocks (26). Because there is no reason for fractionation of Os isotopes between volcanic aerosols and rocks, the average aerosols likely have Os values closer to ≈ 0.53 (25). If so, subaerial volcanism may not be the primary source of Os in precipitation.

Anthropogenic Contributions of Osmium in Precipitation. Industrial ore processing produces OsO_4 because of high temperatures and oxidizing conditions. In sulfide ore (base-metal and PGE) processing, OsO_4 is generated during the converting phase, where S is removed as SO_2 by the passage of hot air/oxygen through the molten ($900\text{--}1,250\text{ }^\circ\text{C}$) matte that contains mainly metal plus S (9, 38). Scrubbing of the exhaust gases to remove SO_2 appears to nearly quantitatively remove OsO_4 . The majority of OsO_4 is trapped either by the wash sulfuric acid or the slime produced during scrubbing (39). The SO_2 can be used in sulfuric acid production, where the SO_2 is oxidized to SO_3 and then dissolved in H_2SO_4 to form oleum, which is then diluted to form sulfuric acid. Any remaining OsO_4 in the washed SO_2 gas is likely sequestered during sulfuric acid production. The amount of base-metal sulfide ore processed annually is vastly greater than PGE ores, but most base-metal processing facilities appear to scrub for SO_2 (40), whereas PGE ore facilities do not (34). This indicates that processing of PGE ores could release Os observed in precipitation. Indeed, the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the unradiogenic endmember from the mixing trend (Fig. 2) directly matches the isotope composition of PGE ores from Merensky Reef, South Africa and Noril'sk, Russia (Fig. 1). Chromites have high Os contents, and chromite smelters are known to emit Os (14). However, chromites are a less likely source because their Os isotope compositions are much lower than those found in the precipitation samples, and the Os seems to precipitate out close to the source (14). The localized deposition may be due to shorter smokestacks because chromite smelters do not emit SO_2 .

We estimate that Os released from the current production and usage of Pt would result in precipitation with a concentration of $\approx 9\text{ fg g}^{-1}$. This is based on global annual Pt production of 217,000 kg (2005 value) (41) and Pt/Os for PGE ore of ≈ 50 (42), and assuming all Os in PGE ore was volatilized to the atmosphere and ended up in precipitation during production and/or use. It is of the same order of magnitude as the Os concentrations measured in our precipitation samples. Both the exhaust from automobile catalytic converters (17) and the refining of PGEs could provide Os to the atmosphere with the same $^{187}\text{Os}/^{188}\text{Os}$ ratio as that inferred for the unradiogenic precipitation end member. The estimated upper limit of anthropogenic Os flux from automobile exhaust is $\approx 120\text{ pg m}^{-2}\text{ y}^{-1}$ (17), which would result in precipitation with an Os concentration of $\approx 0.1\text{ fg g}^{-1}$. It follows that automobile exhaust provides only a minor source of anthropogenic Os to the atmosphere, with refining of PGEs as the primary source.

That volatility of OsO_4 may be controlling the transport of Os in the atmosphere can be assessed by examining its atmospheric enrichment factor. An atmospheric enrichment factor (AEF) is defined as: $\text{AEF} = \log\{([\text{Os}]_{\text{atm}}/[\text{Al}]_{\text{atm}})/([\text{Os}]_{\text{cont}}/[\text{Al}]_{\text{cont}})\}$, where the subscripts *atm* is atmosphere, and *cont* is upper continental crust. For volatile trace elements, there appears to be a negative relationship between the boiling point of the oxide and its AEF (43), i.e., the lower the boiling point of an element, the higher its AEF. For an OsO_4 boiling point of $135\text{ }^\circ\text{C}$, the

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